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Enclosure 1

## Statement of the problem studied

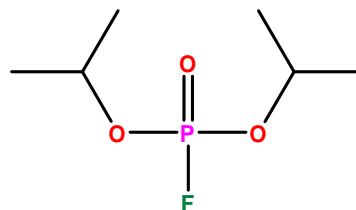
While the electrochemical  $\text{ClO}_2$  generation technology reported previously provides an effective decon system for mustard, VX and biological agents it is ineffective against G-agents. The main focus of this work has been the incorporation of further chemistry into the current decon system to provide a universal field decontamination system. This required the identification of a suitable nucleophile to attack G-agent via nucleophilic substitution. The choice of nucleophile is not a trivial one as several criteria need to be met. The ideal choice would be highly reactive towards G-agent, stable over long storage periods, not persist in the environment after use and be cheap and readily available.

## Summary of the most important results

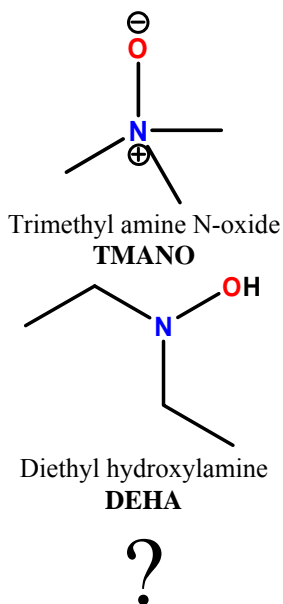
Research has shown that rapid decontamination of G-agent can be achieved using the hypobromite ion ( $T_{1/2} = 1$  min). This nucleophile is also generated electrochemically from aqueous solution containing NaBr. Initial results suggest that this hypobromite technology can be easily incorporated with the current  $\text{ClO}_2$  system to produce a decon system for use against all chemical and biological warfare agents.

## Summary of previous work

Several nucleophiles were screened for activity towards the G-agent simulant diisopropylfluorophosphate (DFP) (**Figure 1**). These nucleophiles were tested here at P&G and against live G-agent at Edgewood Chemical and Biological Center (ECBC). While several nucleophiles were found to show activity towards DFP, many of them proved to be reactive with  $\text{ClO}_2$  itself and so could not be incorporated into the system. Some of the lead



**Figure 1.** Structure of DFP, chemical stimulant used at P&G for G-agent studies.

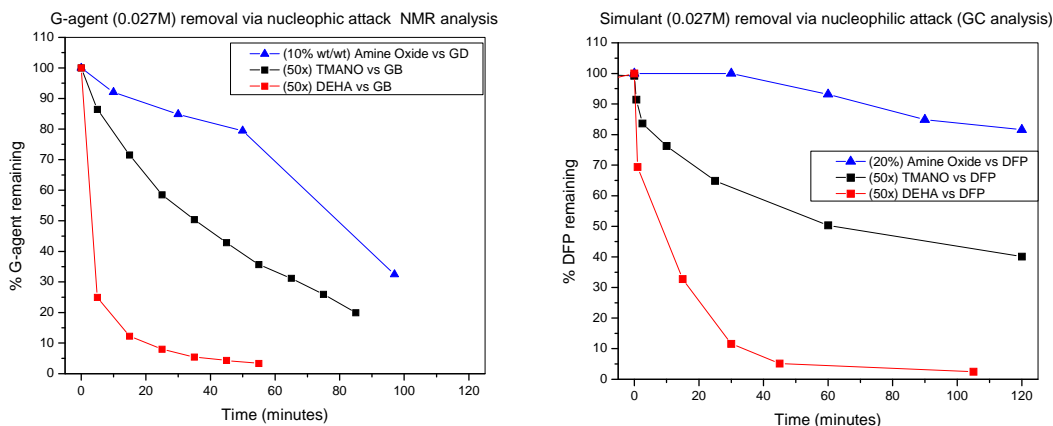


P&G amine oxide

**Figure 2.** Some of the lead nucleophiles tested.

nucleophiles are shown in **Figure 2**. As can be seen from **Figure 3**, there is good correlation between the simulant and live agent testing suggesting DFP is a suitable simulant for G-agents. The nucleophile, DEHA, showed rapid removal of G-agent with  $T_{1/2} < 10$  minutes. Unfortunately, DEHA proved to be highly reactive with  $\text{ClO}_2$ , so much so that when these reagents were mixed, the oxidative activity towards mustard, VX and biological agents was lost. The most active nucleophile found that remained compatible with the chlorine dioxide technology was TMANO. This molecule was stable in the presence of  $\text{ClO}_2$ , but this stability was traded off against efficacy, with  $T_{1/2}$  increasing to approximately 30 minutes. While TMANO showed reasonable decon rates towards G-agent, a  $T_{1/2}$  of 10 mins

(preferably 5 mins) is a target for immediate decon. These results highlight the difficulty



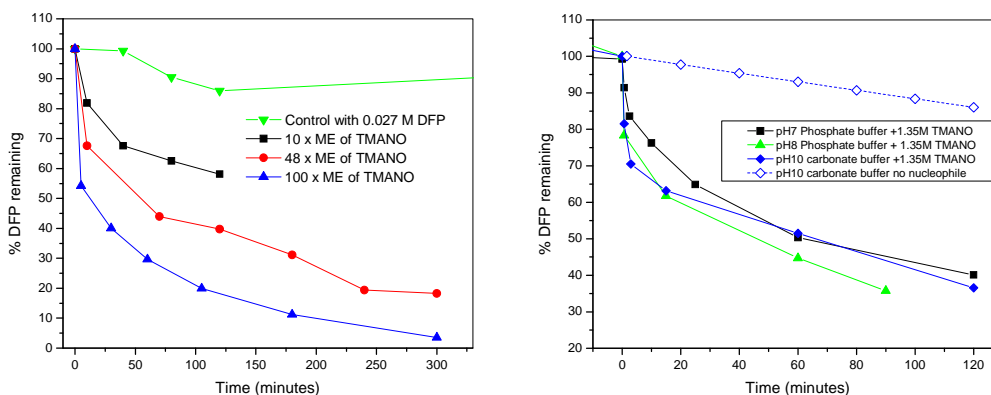
**Figure 3.** Plots showing removal of G-agent (left, measure at ECBC) and DFP (right, measure at P&G) over time with various nucleophiles in aqueous solution.

in maintaining the balance between stability and high reactivity, both of which are vital to develop a potent, universal decon system.

## Current work

### Standard nucleophiles

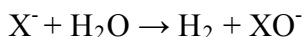
As a large number of common, off the shelf nucleophiles had been tested, the synthesis and testing of new nucleophiles was proposed. This route was not pursued however on the basis of the financial and time investment required. Methods of improving the reaction rate of the stable nucleophile TMANO with G-agent were also researched further at P&G. The TMANO loading and pH (Figure 4) of the decon solution were both varied in an effort to improve efficacy. Ultimately, the  $T_{1/2}$  value remained in the order of tens of minutes, an order of magnitude greater than that required.



**Figure 4.** Variation in molar excess (ME) of TMANO loading on DFP removal (left plot). The right plot shows the effect of pH on the removal of DFP using TMANO.

### Electrochemically generated nucleophiles

As mentioned above, the need for high activity and stability, may at first glance appear to be mutually exclusive. However, technology used within another P&G project suggested an intriguing alternative. The idea was essentially the same as that used for  $\text{ClO}_2$ . Rather than incorporate a nucleophilic molecule into the decon mixture prior to electrolysis, the electrical potential could be used to generate an active nucleophile at the electrodes when required. The nucleophiles that had been investigated at P&G were the hypohalites that can be formed electrochemically from a salt solution of  $\text{NaX}$ , where X is the halide (Cl, Br or I) according to **Equation 1**.

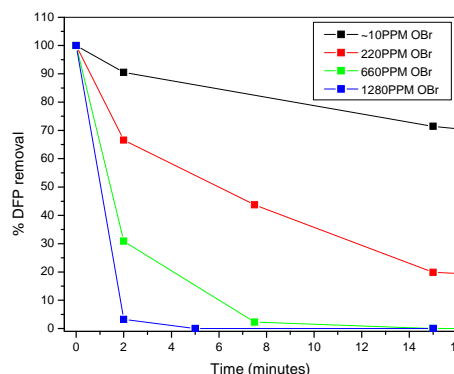


**Equation 1**

The chloro, bromo and iodo halites were all tested against DFP to evaluate their potential. Hypoiodite was found to be unstable and decomposed in a matter of minutes. This would not necessarily be a problem providing the  $\text{IO}^-$  could rapidly react with DFP. Unfortunately, hypoiodite showed poor neutralization efficacy and no further studies were made on this species.

Hypochlorite and hypobromite both showed greater stability when compared with the iodo analogue. Studies carried out against DFP using equal concentrations of  $\text{BrO}^-$  and  $\text{ClO}^-$  showed the bromine derivative to be the more active.

The effect of hypobromite loading upon neutralization rate was investigated by passing solutions containing increasing concentrations of  $\text{NaBr}$  through the electrochemical cell. The amount of oxidant generated was measured using a HACH calorimeter and the progress of the reaction was followed using GCMS. The results are shown in **Figure 5** which clearly demonstrates the rapid neutralization caused by the hypobromite. At  $\text{BrO}^-$  levels of 600 ppm and upwards a  $T_{1/2}$  of between 1 and 2 minutes is observed.



**Figure 5.** Effect of  $\text{BrO}^-$  concentration on DFP removal.

In order for the hypobromite to act as an efficient nucleophile it has to be present in solution in its deprotonated form. Hence, in order for decontamination of G-agent to be effective, the pH of the system has to be maintained above 8.6 which is the  $\text{pK}_a$  value of the hypobromite. This pH requirement is fulfilled in that the dissolved sodium chlorite already present in the solution helps to maintain a pH around 10. As mentioned above, although hypochlorite showed slightly less activity towards DFP it has a lower  $\text{pK}_a$  value than hypobromite. This could be used to provide a system that maintains activity towards G-agents in more neutral conditions.

Initial studies also suggest there is little interaction between the two electrochemically generated species ( $\text{ClO}_2$  and  $\text{BrO}^-$ ). Measurement of the total oxidant levels from the mixed salt solution seems to be additive of what is expected from the amount of each salt present.

## **Conclusions**

The hypobromite ion has been shown to be a highly effective nucleophile that has excellent reactivity towards G-agent. A great benefit of using this species is that it can be easily incorporated into the current electrochemical technology, simply by adding NaBr to the current sodium chlorite solution. This methodology allows the use of stable, cheap precursors that can be shipped as a dry powder making transportation logistics much easier. Addition of water followed by electrochemical activation when decontamination is needed then provides the reactive chemistry required to neutralize any chemical or biological agents present. This 'chemistry on demand' approach is extremely desirable.

## **Future Work**

Work will be undertaken to design the optimum salt composition ( $\text{NaClO}_2$  and NaBr) for use in a final, 'one solution for all contaminants', formulation. This work will involve carrying out multivariate analysis testing on the oxidant levels produced for a broad range of mixed salt solutions. These results will be evaluated alongside decon testing on simulants here at P&G and on live agents at ECBC.

The inclusion of surfactants into the decon system will also begin during the next year. These will aid in cleaning, especially with regards to thickened agents. A good surfactant blend would help disperse thickened agent in solution and increase the decon rate. Naturally, these surfactants will have to be compatible with the electrochemical technology and be unreactive towards the oxidants it produces. Although this task is not trivial, P&G has extensive experience in this field and is confident in formulating a successful blend.

Finally, P&G will continue to work with companies to improve the electrochemical cell technology. This will involve testing various generations of prototype cell with a view to increasing efficiency and minimizing cost. It will also provide valuable information on how to scale-up the technology for use in larger decon systems. In theory, these would have the potential to be retro-fitted into some of the military's current equipment.